

Ternary and quaternary mixed electrolytes for lithium cells

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This paper reports the influence of composition of mixed solvent electrolyte composition on the discharge capacity and charge–discharge cycle life of lithium metal/amorphous V_2O_5 – P_2O_5 (95:5 in molar ratio) cells. The solvents used were ethylene carbonate (EC), propylene carbonate (PC), 2-methyltetrahydrofuran (2MeTHF) and THF. $LiAsF_6$ was used as the solute. The electrolyte solutions examined here contain ternary and quaternary mixed systems. The purpose of this work is to obtain an electrolyte solution which realizes a higher rate capability and/or a longer cycle life than the previously studied EC:PC:2MeTHF (15:70:15) ternary mixed system. Of the electrolyte systems examined here, the EC:PC:2MeTHF (30:40:30 in volume) ternary mixed solvent system showed the best cell performance. In addition, a heating test was carried out on an AA-size lithium cell with EC:PC:2MeTHF (30:40:30) as a fundamental abuse test to ensure cell safety.

Keywords: *lithium, rechargeable battery, organic electrolyte, ethylene carbonate, propylene carbonate*

1. Introduction

Much research has focused on the influence of non-aqueous electrolyte materials on the performance of cells with lithium metal anodes [1–5]. With the lithium metal battery system, the most important problems to be solved are those related to cycle life, rate capability and safety. These problems are closely related to the selection of a suitable electrolyte for a given cell system. Previous works [4–6] have shown that the use of ether compounds as electrolyte solvents is effective for realizing high cycling efficiency with lithium anodes [4–6]. Many ether solvents are difficult to use for 4 V cell systems because their oxidation potential is lower than 4 V vs Li/Li^+ [1]. However, it has also been found that there are many ether solvents useful for 3 V cell systems [1–6]. However, in terms of mass production, it is difficult to use large amounts of ether compounds because of such factors as cell safety, electrolyte cost and handling in the manufacturing plant. Ethers have low flash and boiling points, easily produce dangerous peroxides and are expensive. For instance, while the respective flash points (FP) of ethylene carbonate (EC) and propylene carbonate (PC) are 130 and 160 °C, the FP of 2-methyltetrahydrofuran

(2MeTHF) is –11 °C [6]. 2MeTHF is approximately seven times more expensive than EC or PC [7]. For these reasons, we have examined electrolytes with a maximum 2MeTHF content of 15 vol % [5] and found that a cell with $LiAsF_6$ –EC:PC:2MeTHF (15:70:15) ternary mixed solvent electrolyte exhibits a long cycle life when it has a lithium metal anode and an amorphous (a)- V_2O_5 – P_2O_5 (95:5 in molar ratio) cathode (Li/a- V_2O_5 cell) [5].

In this report we examine the influence of the electrolyte composition of EC:PC:2MeTHF-ternary or EC:PC:2MeTHF:THF quaternary mixed electrolytes on the cell performance of lithium metal cells in order to obtain an electrolyte system which has a higher rate capability and a longer cycle life than the EC:PC:2MeTHF (15:70:15) ternary mixed solvent electrolyte examined in a previous study [5]. In this work we examined electrolytes containing in the 10 vol % to 30 vol %. We used $LiAsF_6$ as the solute. The abbreviations and compositions of the mixed solvent electrolytes examined here are shown in Table 1. A coin type Li/a- V_2O_5 cell was used in order to evaluate the influence of different electrolytes on the rate capability and the cycle life. An abuse test was carried out on an AA-size Li/a- V_2O_5 cell.

Table 1. Electrolyte abbreviations used in this report (1 M LiAsF₆)

Electrolyte abbreviation Type	Solvents (vol %)			
	EC	PC	2MeTHF	THF
A	15	70	15	—
B	50	—	50	—
C	30	40	30	—
D	15	55	30	—
E	15	65	15	5
F	15	70	10	5
G	10	75	10	5
H	5	85	5	5
I	15	60	15	10
J	15	55	15	15
K	10	90	—	—

2. Experimental details

2.1. Electrolytes

The electrolyte solutions were prepared as described in previous papers [4–6]. The water content was less than 20 ppm. Hereafter, ‘1 M LiAsF₆–EC:PC:2MeTHF:THF (15:70:10:5)’ will represent an electrolyte solution composed of mixed EC, PC, 2MeTHF and THF solvents (mixing volume ratio 15:70:10:5) dissolved in 1 M LiAsF₆. The volume percentage is expressed to give a total of 100. In some places different expression is used for the mixing ratio of the solvents. For example, ‘1 M LiAsF₆ EC(15):PC:2MeTHF:THF(30)’ represents an electrolyte solution composed of mixed EC, PC, 2MeTHF and THF solvents where the EC content is 15 vol %, the THF content is 30 vol %, and the total amount of PC and 2MeTHF is 55 vol %. The electrolyte conductivity was measured at 1 kHz with an LCR bridge (Gen Rad Co., model 1658).

2.2. Fabrication of Li/a-V₂O₅ cell

A coin-type cell (2 mm thick × 23 mm diam.) was used for the charge and discharge tests and its structure is shown in Fig. 1. Figure 2 shows a typical charge–discharge voltage curve of a Li/a-V₂O₅ coin cell. This cell has a sandwiched electrode structure composed of a lithium metal foil anode (150 μm thick), a polypropylene separator (25 μm thick), and a printed cathode sheet of a-V₂O₅–P₂O₅, a polymer binder and conductive carbon (130 μm thick includ-

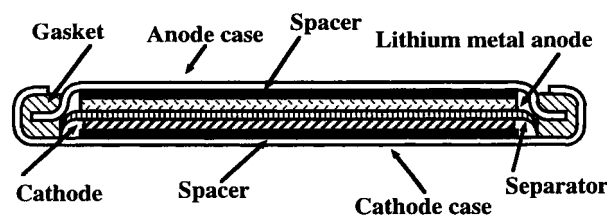


Fig. 1. Coin cell structure.

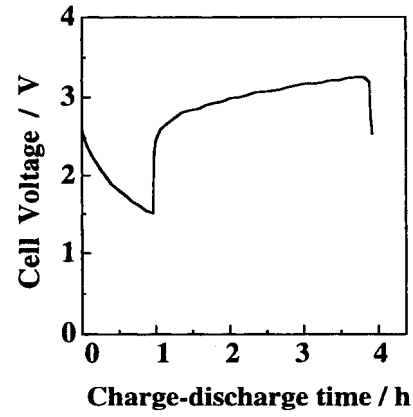


Fig. 2. Change–discharge voltage curve of a Li/a-V₂O₅ coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm^{−2} and a charge current density of 1 mA cm^{−2}, with type-A electrolyte defined in Table 1 [1 M LiAsF₆–EC:PC:2MeTHF(15:70:15)].

ing the cathode substrate). The electrode surface area is 2 cm². a-V₂O₅–P₂O₅ (95:5 in molar ratio i.e., 95 mol % V₂O₅) was prepared by melting raw reagent-grade oxides in platinum crucibles for an hour at 750 °C, and then quenching them on a water-cooled iron block [8]. There is long distance of about 1.2 mm between the electrodes in this coin cell. Stainless steel spacers, 0.4 and 0.8 mm thick were placed on the anode and cathode sides, respectively, as shown in Fig. 1, to apply stack pressure on the lithium anode [9]. The stainless steel spacers (0.4 and 0.8 mm thickness on the anode and cathode side, respectively) is placed as shown in Fig. 1.

Charge–discharge cycling tests were carried out galvanostatically on the coin cells between a charge cut-off voltage of 3.3 V and a discharge cut-off voltage of 1.5 V. The discharge current density had a high rate of 6 mA (3 mA cm^{−2}) and the charge current density had a quick charge rate of 2 mA (1 mA cm^{−2}). The cell operation temperature was 21 °C unless otherwise noted. The cycle life of the cells was evaluated by the figure of merit (FOM) defined in Equation 1 [10], by setting the end of life (EOL) at the cycle number where the discharge capacity become 50% of the maximum value. The FOM is related to the cycling efficiency of the lithium anode (E_{ff} , %) as shown in Equation 2 [11]. In this cell, the capacity of the cell is initially cathode limited but the cycle life is determined by that of the lithium anode:

FOM

$$= \frac{[\text{accumulated discharge capacity}]}{[\text{theoretical capacity of Li initially put into the cell}]} \quad (1)$$

$$\text{FOM} = \frac{100}{(100 - E_{ff})} \quad (2)$$

In this work the rate capability of the cell is evaluated by the cathode utilization defined in Equation 3. If the AA cell is fabricated with a 200 cm² cathode sheet, its capacity is calculated to be 600 mA h. Then,

for this cell, 0.58 mA is equal to a 10 h discharge rate (0.1 C rate):

Cathode utilization

$$= \frac{[\text{discharge capacity at a given discharge current}]}{[\text{discharge capacity at } 0.58 \text{ mA}]} \quad (3)$$

The cell capacity at a discharge current of 6 mA (3 mA cm^{-2}) is approximately 6 mA h. If the AA cell is fabricated with a 200 cm^2 cathode sheet, its capacity is calculated to be 600 mA h. Then, for this cell, 3 mA cm^{-2} represents the 1 h discharge rate (1 C rate). The cell capacity at 0.58 mA (0.29 mA cm^{-2}) discharge is approximately 6.5 mA h and this capacity does not depend on the electrolytes mentioned above. The maximum discharge current used here is 10 mA (5 mA cm^{-2}). In addition, the charge current density of 1 mA cm^{-2} represents the 3 h charge rate ($1/3$ C rate).

Figure 3 shows an example of the stack pressure effect on the cycle life of Li/a- V_2O_5 cells. Figure 4 shows an example of the stack pressure effect on the rate capability of a Li/a- V_2O_5 cells. Cells (a) and (b) shown in Figs 3 and 4 are cells with and without a spacer, respectively. The electrolyte is 1 M LiAsF₆-EC:PC:2MeTHF (15:70:15), 'type A electrolyte' defined in Table 1. The cycle life of cell (a) was 433 cycles while that of cell (b) was 124 cycles. The FOM of cell (a) was 20, which was five times larger than that of the cell (b). Also, the rate capability of the cell (a) was better than that of cell (b). This stack pressure effect was generally obtained for the cells whatever the electrolytes. All the experimental results provided below are for coin cells with a spacer.

2.3. Abuse test

The heating test we used involved placing a cell into a preheated oven [4]. The test cell was an AA-size Li/a-

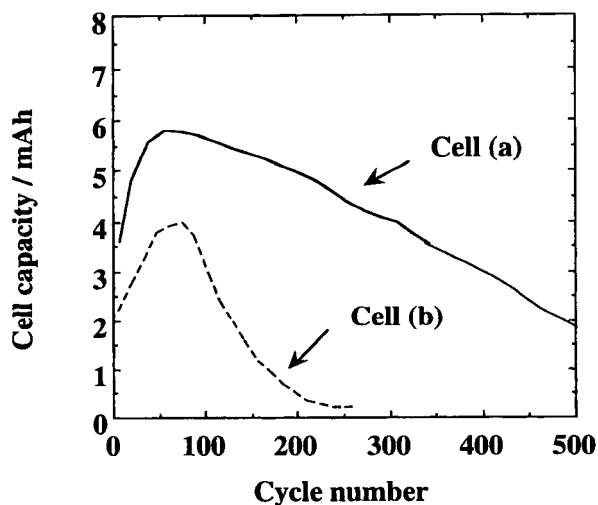


Fig. 3. Cycling test results for Li/a- V_2O_5 coin cells with 1 M LiAsF₆-EC:PC:2MeTHF (15:70:15) cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm^{-2} and a charge current density of 1 mA cm^{-2} , cell (a) with spacer; cell (b) without spacer.

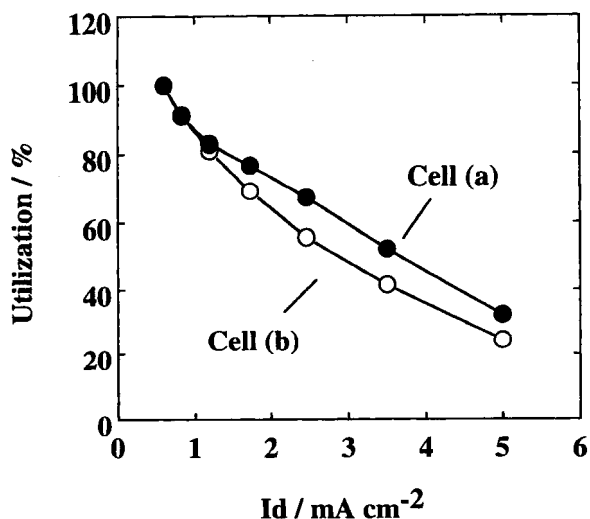


Fig. 4. Relationship between cathode utilization and discharge current density (I_d) for a Li/a- V_2O_5 coin cell with 1 M LiAsF₆-EC:PC:2MeTHF (15:70:15), cell (a) with spacer; cell (b) without spacer.

V_2O_5 cell whose capacity was about 600 mA h. This cell was fabricated by winding a lithium anode sheet, a cathode sheet and a polyethylene separator sheet together and had a safety pressure vent at the bottom of the cell can.

3. Results and discussion

3.1. EC:PC:2MeTHF:THF quaternary mixed electrolyte

In this section we describe experimental results concerning the influence of the composition of EC:PC:2MeTHF:THF quaternary mixed electrolyte on the rate capability and charge-discharge cycle life of a Li/a- V_2O_5 cell.

First, we describe the influence of the THF content in an EC:PC:2MeTHF:THF quaternary mixed electrolyte. Figure 5 shows the relationship between electrolyte conductivity (κ), temperature and THF content in 1 M LiAsF₆-EC(15):PC:2MeTHF(15):THF mixed electrolyte. The letters in Fig. 5 correspond to the type of electrolyte defined in Table 1. Both the EC and 2MeTHF content is 15 vol%, which is the same as in the previously examined EC:PC:2MeTHF ternary electrolyte (type-A electrolyte in Table 1) [5]. Both the content of EC and 2MeTHF is 15 vol%, which is the same as the EC:PC:2MeTHF ternary electrolyte (type-A electrolyte in Table 1) previously examined [5]. Since the remaining solvent components are PC and THF, the total amounts of the ether solvents (THF + 2MeTHF) increase and the amount of PC decreases as the THF content increases in the quaternary systems shown in Fig. 5. The conductivity is measured between -20 and 60°C , which is the usual operating temperature range for commercially available lithium cells. As shown in Fig. 5, the conductivity of quaternary mixed electrolyte is higher than

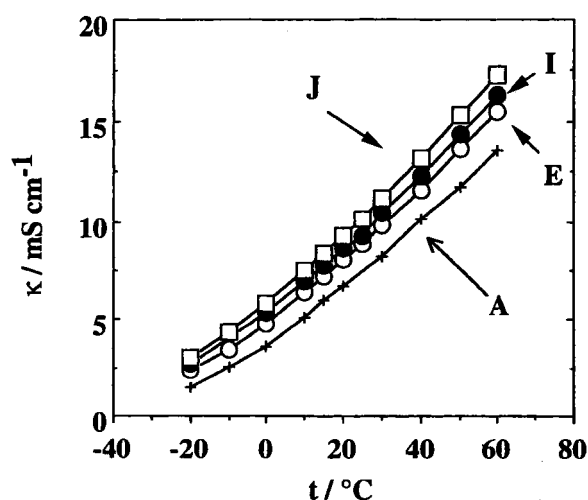


Fig. 5. Relationship between temperature (t) and conductivity (κ) of 1 M LiAsF₆-EC(15):PC:2MeTHF(15):THF electrolytes defined in Table 1.

type-A electrolyte and the conductivity increases with an increase in the THF content in EC:PC:2MeTHF:THF electrolytes. The reason is as follows. The electrolyte conductivity is proportional to the product of the number of ions and their diffusion rate. These two factors are influenced by the dielectric constant and the viscosity of the solvents [12]. However, it was found that there is no distinct relationship between electrolyte conductivity and dielectric constant when lithium salts with large anions, such as LiAsF₆, are used and the reduction in the viscosity is a dominant factor determining the improvement in the conductivity for the electrolyte solutions examined here [4,13,14]. For example, the solvent viscosity must be less than 1.5 cP in order to obtain 10 mS cm⁻¹ around 20 °C from an electrolyte solution with LiAsF₆ [13,14]. The main reason for the improvement in the conductivity with an increase in ether content is therefore considered to be the decrease in solvent viscosity.

Figure 6 shows the relation between THF content and cathode utilization or the FOM of the Li/a-V₂O₅ cell. The cathode utilization shown in Fig. 6 is that at a discharge current density (I_d) of 5 mA cm⁻², which is the highest value tested in this work. The cathode utilization increases with increase in THF content. As shown in Fig. 5, the electrolyte conductivity increases with increase in THF content. This reveals that enhancing the electrolyte conductivity is an effective way of improving cathode utilization. The FOM decreases while the utilization increases with increase in THF content. The FOM decreased greatly when the THF content exceeded 10 vol%. So, based on the results both of the rate capability (cathode utilization) and the cycle life (FOM), THF content must be suppressed to less than 10 vol% in EC:PC:2MeTHF:THF mixed systems. The reason why for the FOM decrease with increases in THF content is considered to be as follows. All the organic solvents reacts thermodynamically with lithium [12]. However, in many cases, the reaction products form an

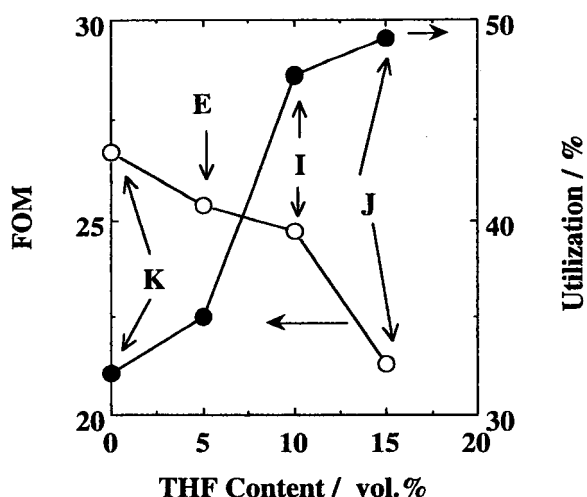


Fig. 6. Relationship between THF content and cathode utilization or FOM for a Li/a-V₂O₅ coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm⁻² and a charge current density of 1 mA cm⁻² with EC(15):PC:2MeTHF(15):THF electrolytes defined in Table 1.

insoluble surface film on the lithium and this protects the lithium from any further chemical reaction with the electrolyte solution. The problem is that the reactivity of THF toward lithium is very high and it is difficult for reduction product, lithium butoxide, to form a surface film since it is soluble in THF of concentration greater than 1 M [15]. For this reason, there is a large difference between the lithium cycling efficiencies of THF and 2MeTHF. For instance, the cycling efficiency of lithium in a single solvent electrolyte incorporating LiAsF₆ as the solute is 96.4% for 2MeTHF and 88.0% for THF [16]. That is, the FOM of 2MeTHF (27.7) is 3.3 times larger than that of THF (8.3). While the difference in the FOM is smaller than for single solvent electrolytes, its reduction with increase in THF content is also reported in mixed solvent electrolytes, such as THF:2MeTHF [12] or EC:2MeTHF:THF ternary systems [17]. This phenomenon is interpreted as originating from the fact that there is a higher concentration of THF around the interface between the electrolyte solution and the lithium anode than with the bulk electrolyte composition [12, 14].

Figure 7 shows the relationship between electrolyte conductivity (κ) and temperature or 2MeTHF content in LiAsF₆-EC:PC:2MeTHF:THF. Figure 8 shows the relationship between the 2MeTHF content, and the FOM or cathode utilization at 5 mA cm⁻² for a Li/a-V₂O₅ cell. The conductivity and utilization increases with increase in 2MeTHF content as in the case of THF. The reason for the enhancement of the conductivity with increase in 2MeTHF content is due to the effect of the reduction in viscosity. However, the effect of the enhancement on the conductivity and the cathode utilization of 2MeTHF is considerably smaller than that of THF while THF and 2MeTHF are ether solvents with approximately the same viscosity [14]. The reason is the large difference between the conductivities of

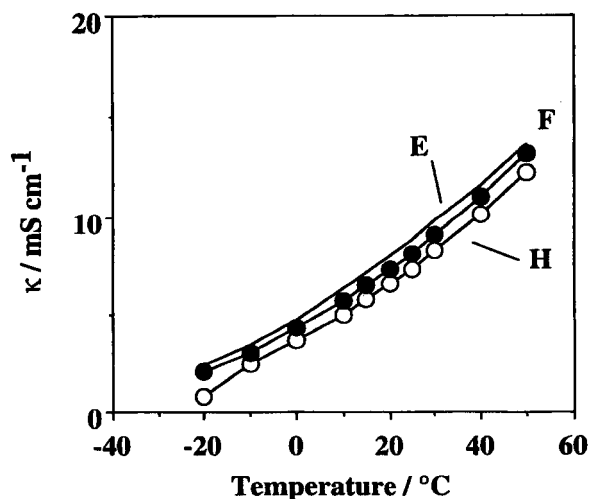


Fig. 7. Relationship between temperature (t) and conductivity (κ) of 1 M LiAsF₆-EC(15):PC:2MeTHF:THF(15) electrolytes defined in Table 1.

THF and 2MeTHF electrolytes. That is, the overall value of the cation and anion conductivity of 2MeTHF electrolyte is lower than that of THF because the practical radius of the 2MeTHF solvated Li⁺ is larger than the Li⁺ solvated with THF [5]. In addition, the lower lithium ion conductivity is disadvantageous for 2MeTHF electrolytes because it affects both the discharge and charge efficiency [4, 17]. Furthermore, the low temperature conductivity is another problem with 2MeTHF electrolyte. That is, LiAsF₆-2MeTHF does not exhibit any practical conductivity below 0°C because the (2MeTHF)_n-LiAsF₆ complex becomes insoluble [17], whereas, the FOM increases with an increase in 2MeTHF content. In regard to conductivity enhancement, THF is much more effective than 2MeTHF. However, in regard to FOM enhancement, 2MeTHF is considerably more effective than THF.

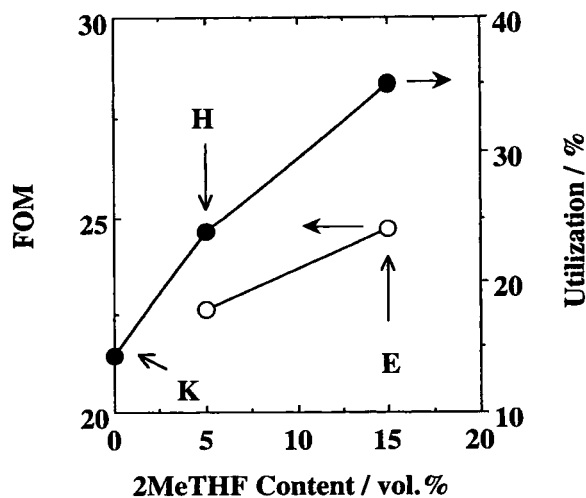


Fig. 8. Relationship between 2MeTHF content and cathode utilization or FOM for a Li/a-V₂O₅ coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm⁻² and a charge current density of 1 mA cm⁻² with 1 M LiAsF₆-EC(15):PC:2MeTHF:THF(15) electrolytes defined in Table 1.

Therefore, the THF and 2MeTHF content of mixed solvent electrolytes containing both solvents must be optimized for battery applications.

The following Section describes the influence of the EC content in EC:PC:2MeTHF:THF quaternary electrolyte. A low EC content is better for a Li/a-V₂O₅ cell system because the reversibility of a-V₂O₅ tends to be worse with increase in EC content because of the solubility problem of Li_xV₂O₅ in EC-based electrolytes [4]. However, the cycling efficiency of lithium increases with increase in EC content [5]. Therefore, we must determine experimentally the optimum EC content for an Li/a-V₂O₅ cell. For instance, the optimum EC/PC mixing ratio is 10:90 for an EC/PC binary mixed solvent electrolyte which contains no ether solvents [4]. Figure 9 shows the relationship between EC content and the FOM or cathode utilization at 5 mA cm⁻² for a Li/a-V₂O₅ cell. The conductivity and cathode utilization increase with increase in EC content. For example, the conductivity of EC:PC:2MeTHF:THF (15:70:10:5), 'type-F electrolyte' defined in Table 1, at 20°C or -20°C is 7.64 mS cm⁻¹ or 2.24 mS cm⁻¹ while that of EC:PC:2MeTHF:THF (10:75:10:5), 'type-G electrolyte' defined in Table 1, at 20°C or -20°C is 7.34 mS cm⁻¹ or 2.06 mS cm⁻¹. With these results, the effect of the high dielectric constant of EC contributes to the increase in the ionic dissociation degree of LiAsF₆. However, the change in conductivity with change in EC content is smaller than that with a change in ether content. As mentioned above, the conductivity is affected much more by the viscosity than by the dielectric constant for an electrolyte solution with a lithium salt having a large anion such as LiAsF₆. The FOM increases with increase in EC content. However, this change is much smaller than that which occurs when there is a change in 2MeTHF content.

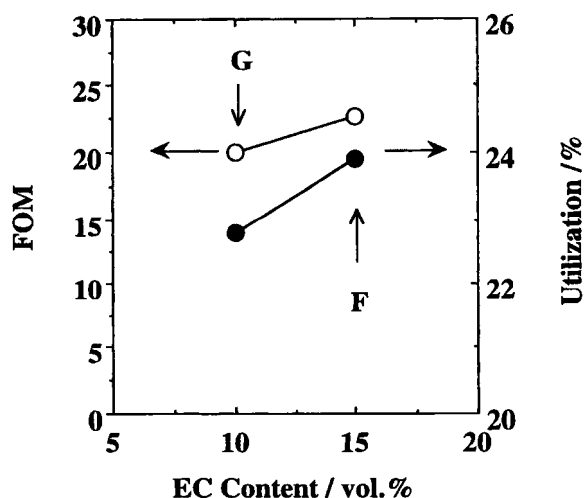


Fig. 9. Relationship between EC content and cathode utilization or FOM for a Li/a-V₂O₅ coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm⁻² and a charge current density of 1 mA cm⁻² with 1 M LiAsF₆-EC:PC:2MeTHF(10):THF(5) electrolytes defined in Table 1.

Judging the influence of the composition of EC:PC:2MeTHF:THF quaternary electrolytes on the cycle life and rate capability of a Li/a- V_2O_5 cell, from a broad perspective, EC:PC:2MeTHF:THF (15:60:15:10) exhibits the best performance. That is, the 2MeTHF, THF or total ether content is 15, 10 or 25 vol %. For battery applications, where a high rate capability is much more strongly required, EC:PC:2MeTHF:THF (15:55:15:15) containing 30 vol % ether solvents, is more suitable. Based on these results, we examined the EC:PC:2MeTHF ternary mixed solvent system containing 30 vol % 2MeTHF and the results are provided in the following Section.

3.2. EC:PC:2MeTHF ternary mixed solvent electrolyte

In our previous investigation of EC:PC:2MeTHF ternary electrolytes [4, 5], the maximum 2MeTHF content was 15 vol %. One of the ternary electrolytes examined here is EC:PC:2MeTHF (30:40:30, type C electrolyte defined in Table 1). In this electrolyte, the EC content is 30 vol % and the EC:2MeTHF mixing ratio is 1:1. This composition was selected because we had already found that the EC:2MeTHF mixing ratio exhibiting the longest cycle life in an EC:2MeTHF binary mixed electrolyte is 1:1 [18]. To evaluate the ability of this type D electrolyte, we compared performance with that of three reference electrolytes. These three electrolytes included type I electrolyte, EC:PC:2MeTHF:THF (15:60:15:10) which exhibited the best performance among the quaternary mixed systems, type A electrolyte, EC:PC:2MeTHF (15:70:15), a standard previously studied electrolyte, and type B electrolyte, EC:2MeTHF (50:50) containing 50 vol % 2MeTHF [18]. Although type B electrolyte is hard to use in practical applications because of its high ether concentration, it was examined as a good reference because it is known to exhibit an excellent FOM and rate capability. The conductivity of these electrolytes is shown in Fig. 10. The order of the enhancement of conductivity is type B > type I > type C > type A electrolyte. With increase in 2MeTHF content the conductivity tends to increase, except for type I electrolyte containing THF. Figure 11 shows the cathode utilization and Fig. 12 shows the FOM of a Li/a- V_2O_5 cell. The cathode utilization tends to increase with increase in conductivity, as already mentioned. The order of increasing FOM is type B > type C > type A > type I electrolyte. The FOM tends to increase with increase in 2MeTHF content, except for type I electrolyte containing THF. The capability of type C electrolyte is described below, compared with that of three reference electrolytes. Compared with type A electrolyte, type C has higher cathode utilization and a higher FOM. Compared with type I electrolyte, type C has a higher FOM and lower cathode utilization. The cathode utilization is 12% lower and the FOM is 23% lower than those of type

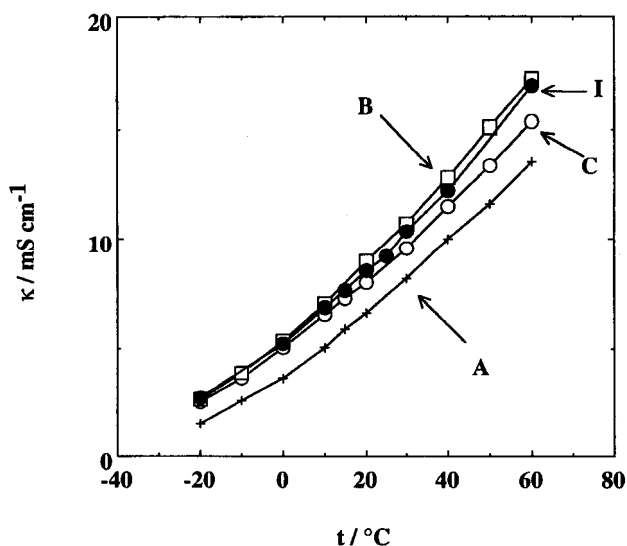


Fig. 10. Relationship between temperature (t) and conductivity (κ) of different electrolytes defined in Table 1.

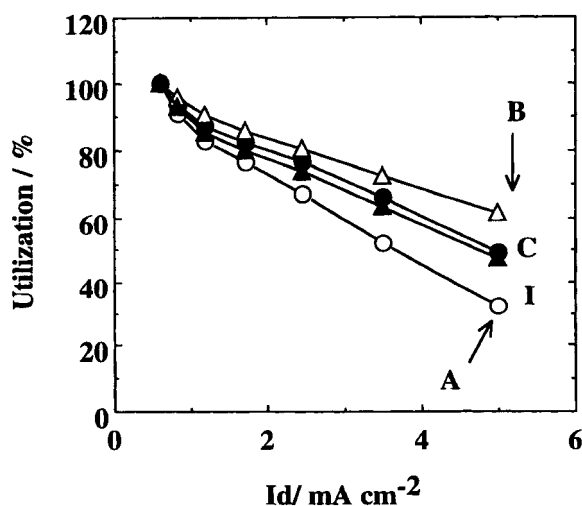


Fig. 11. Relationship between cathode utilization and discharge current density (I_d) for a Li/a- V_2O_5 coin cell with different electrolytes defined in Table 1.

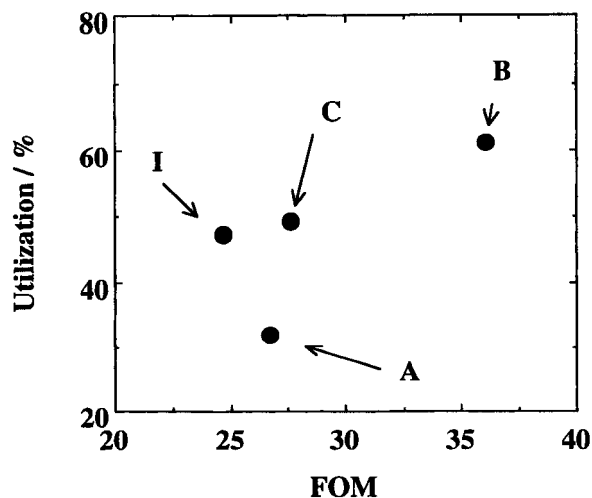


Fig. 12. Relationship between cathode utilization at a discharge current density of 5 mA cm^{-2} and FOM for a Li/a- V_2O_5 coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm^{-2} and a charge current density of 1 mA cm^{-2} with different electrolytes defined in Table 1.

B electrolyte. Therefore, type C electrolyte exhibits the highest FOM and the highest cathode utilization with the exception of type B electrolyte.

3.3. Abuse test

Based on the experimental results on rate capability and cycle life, it was found that type C electrolyte containing 30 vol % 2MeTHF performs better than type A electrolyte, which was formerly used as a standard. However, possible problems remain in terms of cell safety and material cost.

Thermal runaway is a basic problem as regards cell safety. When thermal runaway occurs in a lithium metal cell, the cell ignites [19]. Several exothermic reactions occur inside a cell as its temperature increases. Thermal runaway occurs if heat output exceeds thermal diffusion. The possible exothermic reactions [19] are: (i) the chemical reduction of the electrolyte by the anode, (ii) the thermal decomposition of the electrolyte, (iii) the oxidation of the electrolyte on the cathode, (iv) the thermal decomposition of the anode, and (v) the thermal decomposition of the cathode. It should also be noted that, when a separator melts as a result of its temperature exceeding its melting point ($\sim 125^\circ\text{C}$ for polyethylene and $\sim 155^\circ\text{C}$ for polypropylene), this frequently triggers a large heat output induced by an internal short. In addition, the low melting point of lithium (180°C) helps contribute to a more violent internal short. Since cell safety depends greatly on the individual cell structure, it should be evaluated by using a practical type cell rather than a small coin-type cell. In this study an AA size cell was used for the abuse test.

A heating test by which to ascertain the thermal stability of a cell has been proposed as a fundamental abuse test for a rechargeable battery system with a Li metal anode [4–7]. Wilkinson *et al.* [20] have reported that it is effective to compare the maximum cell temperature resulting from the internal exothermic reaction of AA cells with a 600–800 mA h nominal capacity cycled 25 times at a discharge current of 0.1 C and at a 100% depth of discharge. It is effective to set the heating temperature above the melting point of the separator as this leads to an internal short between the cathode and anode. As the cells fabricated here have a polyethylene separator whose melting point is 125°C , the heating was carried out at 130°C .

Figure 13 shows the results of 130°C heating tests for AA-size Li/a- V_2O_5 cells with 1 M $\text{LiAsF}_6\text{-EC:PC:2MeTHF}$ (30:40:30). The cells were precycled 25 times with a 60 mA discharge and a 60 mA charge between 1.5 and 3.3 V. The Li/a- V_2O_5 cell did not catch fire or vent, although the maximum cell temperature was 150°C which was 15°C higher than that with type-A electrolyte [4]. In addition, the 130°C heating tests were carried out for AA-size Li/a- V_2O_5 cells precycled 50 times with a 600 mA discharge and a 60 mA charge between 1.5 and 3.3 V (Fig. 14). The

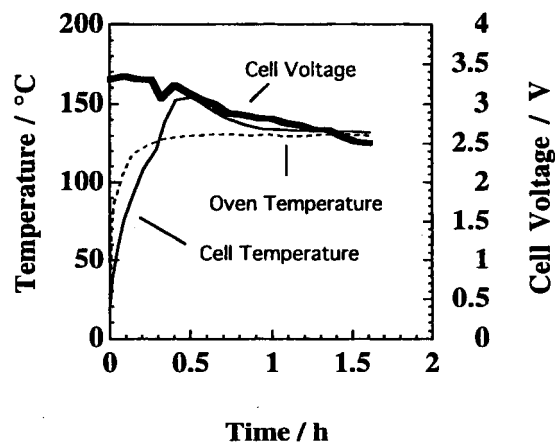


Fig. 13. Heating test result at 130°C for an AA-size Li/a- V_2O_5 cell cycled 25 times with 60 mA charge and 60 mA discharge currents between 1.5 and 3.3 V with 1 M $\text{LiAsF}_6\text{-EC:PC:2MeTHF}$ (30:40:30).

maximum cell temperature was 140°C and the safety vent did not open. Based on the abuse test results described here, an electrolyte containing 30 vol % 2MeTHF can be used in practical applications although the safety decreases with an increase in 2MeTHF content.

It is difficult to predict the actual cost of electrolyte materials for mass produced batteries because this depends on many factors. Therefore, we have made calculations based on the cost of small amounts of reagent [7]. The result is that the material cost of type C electrolyte is 1.5 times higher than type A and double that of EC/PC binary mixed electrolyte without ether solvents.

4. Conclusion

The properties of ternary and four solvent mixed electrolyte are summarized in Figs 15, 16 and Fig. 17. As shown in Figs 15 and 16, the electrolyte conductivity and the cathode utilization of the cells increases with increase in the ether content. In particular, the

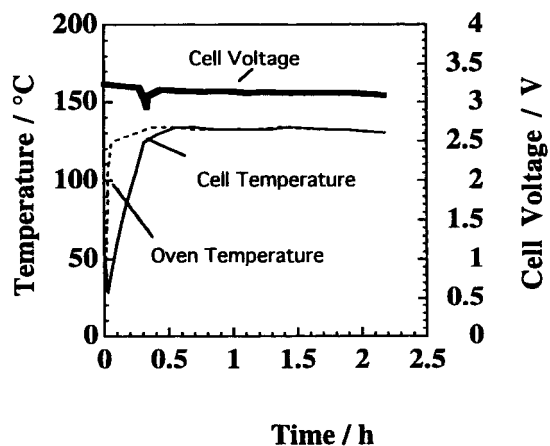


Fig. 14. Heating test result at 130°C for an AA-size Li/a- V_2O_5 cell cycled 50 times 600 mA discharge and 60 mA charge and discharge current between 1.5 and 3.3 V with 1 M $\text{LiAsF}_6\text{-EC:PC:2MeTHF}$ (30:40:30).

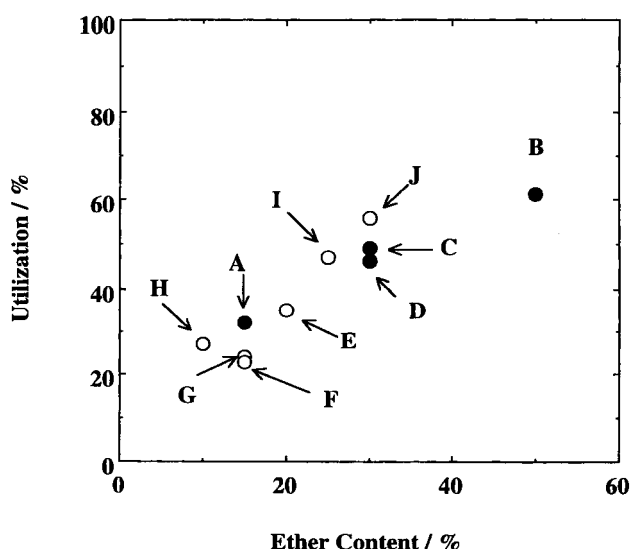


Fig. 15. Relationship between cathode utilization at a discharge current density of 5 mA cm^{-2} and total ether content for a Li/a- V_2O_5 coin cell with different electrolytes defined in Table 1.

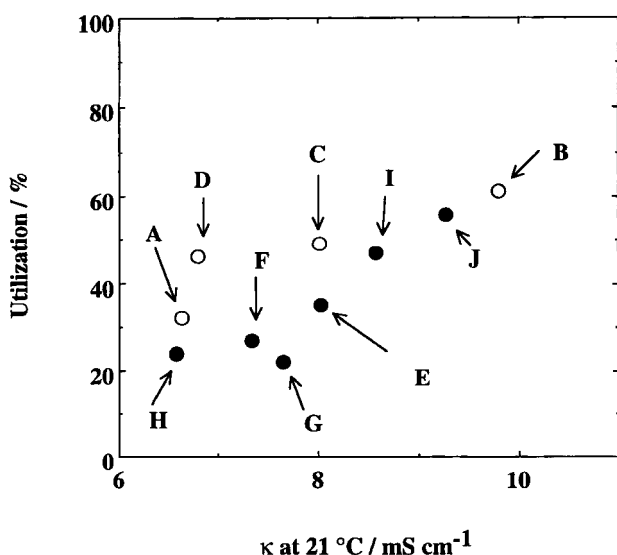


Fig. 16. Relationship between cathode utilization at a discharge current density of 5 mA cm^{-2} for a Li/a- V_2O_5 coin cell and conductivity (κ) of different electrolytes defined in Table 1.

effect of THF is large. With regard to the FOM, this decreased with increase in THF content and also with increase in 2MeTHF content. Summarizing the results of both rate capability and cycle life, EC:PC:2MeTHF (30:40:30) exhibits the best performance among all the ternary and quaternary electrolytes examined in this work. When the stronger requirement is for a good rate capability, EC:PC:2MeTHF:THF (15:60:15:10) or EC:PC:2MeTHF:THF (15:55:15:15) quaternary electrolyte is an effective answer.

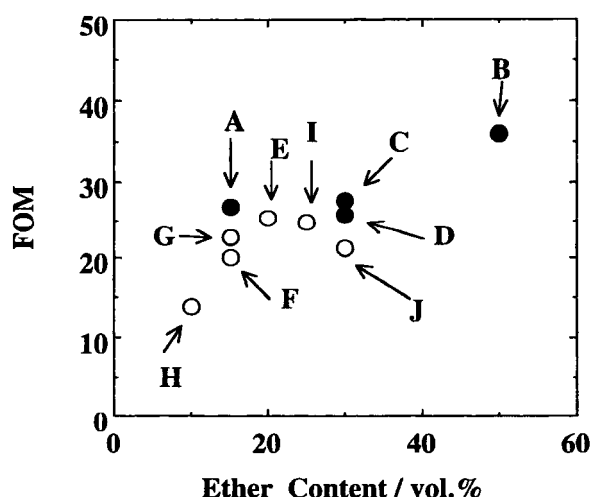


Fig. 17. Relationship between FOM and total ether current for a Li/a- V_2O_5 coin cell cycled between 1.5 and 3.3 V at a discharge current density of 3 mA cm^{-2} and a charge current density of 1 mA cm^{-2} with different electrolytes defined in Table 1.

References

- [1] Y. Matsuda, M. Morita and M. Ishikawa, Extended Abstracts of 8th International Meeting on Lithium Batteries, Nagoya, Japan (1996), p. 29.
- [2] Y. Sasaki, M. Hosoya, M. Handa and Y. Kobayashi, Extended Abstracts of 8th International Meeting on Lithium Batteries, Nagoya, Japan (1996), p. 37.
- [3] H. Nakamura, C. Wang, E. Mitani, T. Fuzita and M. Yoshio, *J. Surf. Finish. Soc. Jpn.* **46** (1995) 1187.
- [4] S. Tobishima, K. Hayashi, K. Saito, T. Shodai and J. Yamaki, *Electrochim. Acta* **42** (1997) 119.
- [5] S. Tobishima, K. Hayashi, Y. Nemoto and J. Yamaki, *ibid.* **42** (1997) 1709.
- [6] S. Tobishima and T. Okada, *Electrochim. Acta.* **30** (1985) 1715.
- [7] Catalogue Handbook of Fine Chemicals, Aldrich Chemical Company, Inc. (1994-1995).
- [8] Y. Sakurai and J. Yamaki, *J. Electrochem. Soc.* **132** (1985) 512.
- [9] T. Hirai, I. Yoshimatsu and J. Yamaki, *ibid.* **141** (1994) 611.
- [10] K. M. Abraham, J. L. Goldman and D. L. Natwig, *ibid.* **129** (1982) 2404.
- [11] J. Yamaki, M. Arakawa, S. Tobishima and T. Hirai, Proc. on 'Lithium Batteries', The Electrochem. Society, PV87-1 (1987), p. 266.
- [12] L. A. Dominey, in 'Industrial Chemistry Library, vol. 5, Lithium Batteries' (edited by G. Pistoia), Elsevier, Netherlands (1994), chapter 4.
- [13] S. Tobishima, M. Arakawa and J. Yamaki, *Electrochim. Acta* **35** (1990) 383.
- [14] S. Tobishima, K. Hayashi, K. Saito and J. Yamaki, *ibid.* **40** (1995) 537.
- [15] V. R. Koch, *J. Electrochem. Soc.* **126** (1979) 181.
- [16] J. L. Goldman, R. M. Mank, J. H. Young and V. R. Koch, *J. Electrochem. Soc.* **127** (1980) 1461.
- [17] K. M. Abraham and J. L. Goldman, *J. Power Sources* **9** (1983) 239.
- [18] S. Tobishima, M. Arakawa and J. Yamaki, *ibid.* **20** (1987) 293.
- [19] S. Tobishima and J. Yamaki, *Prog. Batteries & Battery Mater.* **16** (1997) 309.
- [20] D. P. Wilkinson, J. R. Dahn, U. von Sacken and D. T. Fouchard, Ext. Abstr. ECS Fall Meeting, Seattle, WA, Abstract No. 53, The Electrochem. Society NJ (1990), p. 85.